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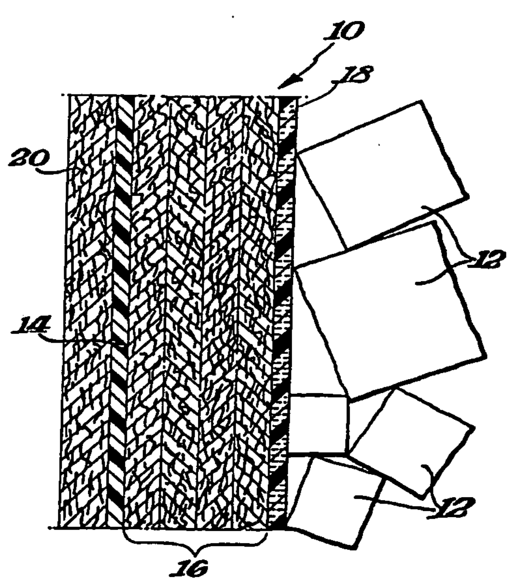
(54) **Packaging of hygroscopic particulates**

(57) A multilayered container for the storage of particulate hygroscopic substances comprises an outer layer 14 having a low water vapour transmission rate and an inner layer 16, of at least one thickness of paper having a moisture content significantly below the paper's equilibrium moisture content. The layer 14 may be of aluminium foil or polyethylene covered by a paper layer 20, and the layer 16 may be covered by a water permeable layer 18 of hydrophobic material.



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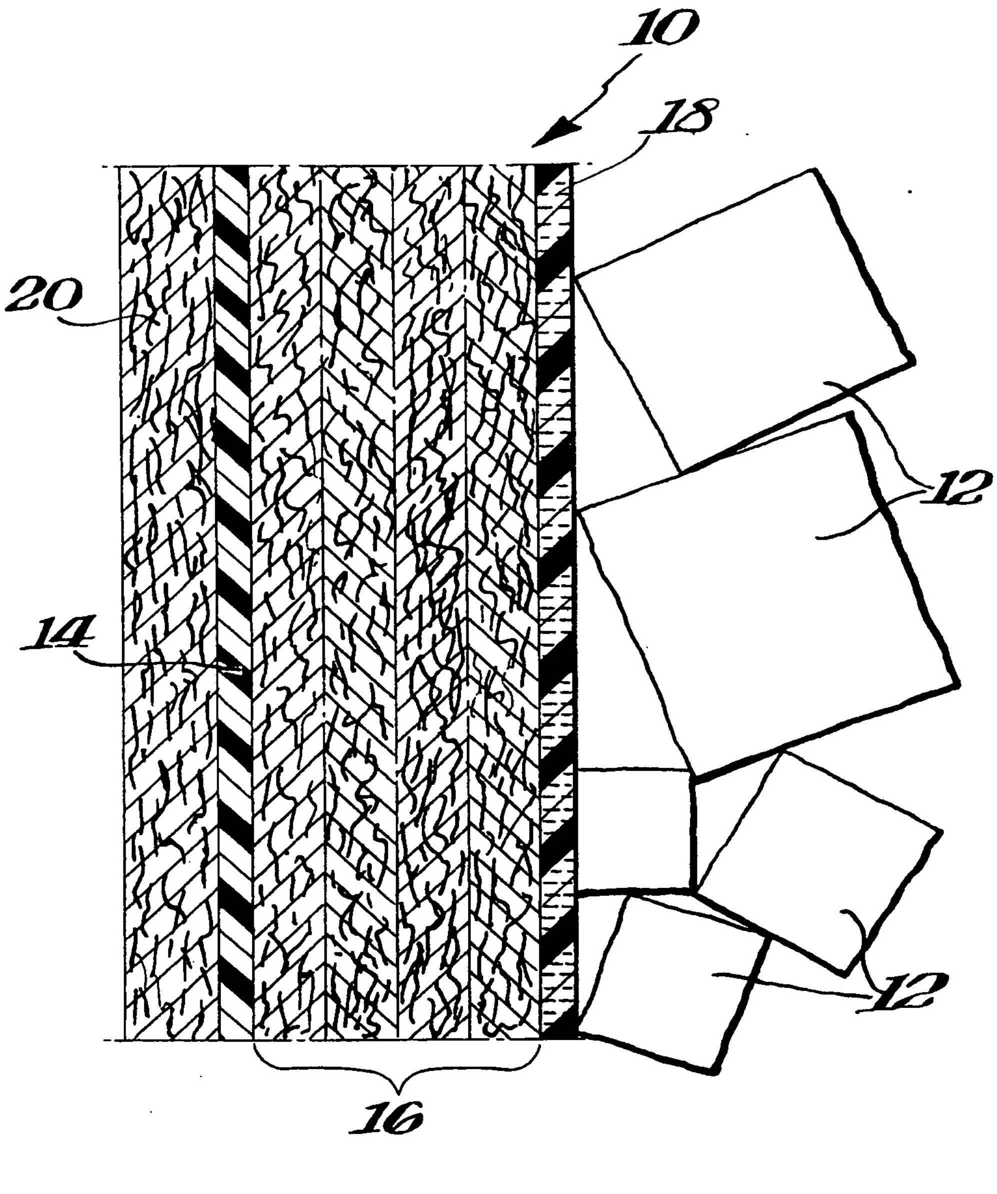

SPECIFICATION

Packaging of hygroscopic particulates

This invention concerns product packaging and storage. More specifically, it concerns a method and container for the packaging and storage of particulate hygroscopic substances such as anhydrous citric acid.

Certain particulate hygroscopic substances such as anhydrous citric acid are extremely sensitive to moisture. Special precautions must therefore be taken during packaging of the product to insure that it remains in particulate form during storage.

For example, anhydrous citric acid is commercially packaged in containers having a low water vapor transmission rate (WVTR) to prevent moisture pick-up from the atmosphere during storage. The product is normally dried atmospherically at elevated temperature and packaged immediately; consequently, the freshly packaged product is slightly above ambient temperature. Although the water content of the packaged product is only in the amount of about 0.1 weight percent, this residual water is sufficient to cause the product particles to agglomerate or lump upon extended storage. It is believed that during cooling, the residual moisture within the crystals tends to migrate to the crystal surface and, since the moisture is prevented from escaping immediately by the impervious nature of the container, condenses to form concentrated solutions between crystals. On continued storage, this moisture eventually escapes and the solid residue effectively joins the individual particles together. If the inside surface of the container is paper, the product also tends to adhere to the container wall for presumably the same reason, and a considerable amount of product can be retained by the container when it is eventually emptied.

In past attempts to minimize this problem a desiccant has been placed within the container to absorb the residual water released from the crystals and thus prevent solution formation. The desiccant customarily is placed in a vapor-permeable pouch generally fastened to the container wall to prevent contamination of the product by the desiccant. While this approach has successfully prevented product lumping, the potential for contamination of the product by the desiccant still exists.

I have found that in those product containers having an inner paper layer, the paper, when dried substantially below its equilibrium moisture content, can itself act as the desiccant for the hygroscopic product.

Accordingly, the present invention provides a multilayered container for the storage of particulate hygroscopic substances which cmprises an outer layer having a low WVTR and an inner layer of at least one thickness of paper having a moisture content significantly below the paper's equilibrium moisture content whereby said inner layer acts as a desiccant for said hygroscopic substances. Preferably, the outer layer comprises aluminium foil or polyethylene film, the outer surface of the outer layer is faced with a layer of paper, the inner surface of the inner layer is faced with a water vapor-permeable layer of a hydrophobic material such as polyethylene, the moisture content of the paper is about 2 to 5 percent by weight below the paper's equilibrium moisture content, the container is in the form of a bag and the hygroscopic substance is anhydrous citric acid.

The invention also provides a method for the packaging of particulate anhydrous citric acid which comprises the step of preparing a multilayered bag comprising an outer layer of low WVTR polyethylene film and an inner layer of at least one thickness of paper faced with a water vapor-permeable layer of polyethylene on the inner surface of the paper layer; reducing the moisture content of the paper in the bag to about 2 to 5 percent by weight below the paper's equilibrium moisture content; introducing the citric acid into the bag and sealing the bag.

The novel features and advantages of the present invention will become apparent from a reading of the following description in conjunction with the accompanying drawing of a preferred embodiment of the invention.

The drawing shows an enlarged fragmental cross-sectional view of a portion of the wall of a multilayered bag suitable for the storage of a particulate hygroscopic substance such as anhydrous citric acid.

Wall 10 includes an outer layer 14 having a low WVTR and an inner layer 16 of at least one thickness of paper. While the drawing illustrates four thicknesses for inner layer 16, as indicated hereinbelow, any convenient number of thicknesses may be used.

The particulate substance 12 being stored may be anhydrous citric acid, the anhydrous forms of its salts such as potassium citrate and anhydrous sodium citrate, or any other particulate substance possessing hygroscopic properties similar to those of anhydrous citric acid. These particulate substances normally have a particle size up to about 3 millimeters.

The low WVTR outer layer 14 of wall 10 serves to minimize the exposure of the particulate substance 12 to outside moisture during storage, especially under adverse conditions of high temperature and high humidity such as may be encountered in the tropics.

The water vapor transmission rate (WVTR), as the term suggests, is a measure of the ease with which water vapor passes through a layer or film. One method of determining the WVTR of a given layer is by exposing one surface of the layer of given area to an atmosphere over anhydrous calcium chloride desiccant and the other surface to a humid atmosphere, and then measuring the moisture pickup of the desiccant during a given period. For the present purpose, the WVTR will be defined as the grams of water transmitted through one square meter of a layer during a period of 24 hours when the humid atmosphere is at 100°F (38°C) and 90 percent relative humidity when following ASTM Standard E96-66 Procedure E (1966).

By low WVTR is meant a WVTR of about 8 or less. The low WVTR layer 14 therefore need only be of such nature to insure that this condition is met.

Preferably the layer 14 will be in the form of a film. The film may be a single component or a composite of two or more components. For example, single films of low density polyethylene (LDPE) having a thickness of about 2 mils (51 microns) or greater, of high density poleythylene (HDPE) having a thickness of about 1 mil (25 microns) or greater and of biaxially oriented polypropylene (BOPP) having a thickness of about 0.75 mil (19 microns) or greater are eminently suitable. Examples of suitable composite films include a laminate formed of polyvinylidene chloride between BOPP having a thickness of about 0.75 mil (19 microns) or greater and a laminate formed of aluminum foil between LDPE having a thickness of about 1 mil (25 microns) or greater.

As illustrated in the preferred embodiment shown in the drawing, the outer surface of outer layer 14 may be faced with a paper layer 20. Such a facing provides a protection for outer layer 14 against mechanical damage such as through abrasion and also provides a surface which is eminently suitable for printing. This paper layer 20 will normally be a single ply having a thickness of from about 5 to 10 mils (127 to 254 microns).

The inner layer 16 comprising at least one thickness, or ply, of paper serves the dual functions of offering an inexpensive means of providing strength to wall 10 and, when dried to a moisture content significantly below the paper's equilibrium moisture content, of acting as a desiccant to absorb both residual moisture from the product and extraneous outside moisture that permeates outer layer 14.

The paper predominantly used in packaging is natural, or unbleached, kraft paper, a strong and relatively cheap paper made chiefly from pine by digestion with a mixture of sodium hydroxide, sodium sulphate, sodium carbonate and sodium sulfide. This paper is customarily supplied in terms of its basis weight, defined as the weight in pounds of a given area of paper; for shipping sack kraft, this area is 3000 square feet (279 square meters). Thus, a 50 pound basis kraft paper is one weighing 50 pounds per 3000 square feet (81 kg per 1000 square meters). Shipping kraft paper is usually 40 to 70 pound basis with corresponding thicknesses of about 3 to 10 mils (76 to 254 microns). Under normal ambient conditions, for example, 70°F (21°C) and 50 to 60 percent relative humidity, the equilibrium moisture content of this kraft paper is about 6 to 8 weight percent. Other papers such as that produced by the holopulping process may also be used with the present invention, the only requirement being that the paper have strength and moisture retention properties similar to that of kraft paper.

More than one ply of paper for inner layer 16 is often used to give the container the capability of holding particulate substance 12 and of resisting breakage and puncture during packaging, shipment and storage. The number of plys will depend upon the amount of particulate substance 12 being stored in the container. For example, four plys are commonly used for bags containing 50 pounds (23 kg) of citric acid, while 5 plys are used for bags containing 100 pounds (45 kg).

To be effective as a desiccant, the paper of inner layer 16 must have a moisture content at the time of packaging significantly below the paper's equilibrium moisture content. By equilibrium moisture content is meant the moisture content of the paper at equilibrium under the ambient packaging temperature and relative humidity conditions. This reduction below the equilibrium value will normally be at least about 1 and not more than about 5 weight percent in terms of the absolute moisture content of the paper. For example, a paper with an equilibrium moisture content of 7 percent by weight would have the moisture content reduced to 6 percent by weight for a 1 weight percent reduction and to 2 percent by weight for a 5 weight percent reduction. A reduction of less than about 1 percent by weight provides the paper with little desiccating capacity, while a reduction beyond about 5 percent by weight may cause the paper to become too brittle for effective use as a storage material. Preferably, the reduction is from about 2 to 5 percent by weight. The reduction can be accomplished in any suitable fashion as, for example, by exposing the paper to an atmosphere of low relative humidity either at elevated or ambient temperature for a period sufficient to attain the desired reduction.

Preferably, as shown in the drawing, the inner surface of inner layer 16 is faced with a water vapor-permeable layer 18 of a hydrophobic material to minimize the tendency of the particulate substance 12 to stick to inner layer 16 of the wall 10 when the particulate substance 12 is removed from the container. The layer 18 may be of any hydrophic material inert to the particulate substance 12 provided the layer 18 is permeable to water vapor. By water vapor-permeable layer is meant a layer having a WVTR of at least about 1500. Suitable layers would include, for example, a porous plastic film such as the family of sheets of spunbonded HDPE fibers supplied by Du Pont under the Registered Trade Mark Tyvek, microperforated polyolefin film, woven polypropylene or the microporous polyolefin film disclosed in British Specification 1,371,833, as well as a thin coating or deposit of polyolefin such as polyethylene on the inner surface of inner layer 16 which incompletely seals the layer, such as disclosed in British Specification 1,412,144. Normally the water vapor-permeable layer 18 will have a thickness of up to about 10 mils (254 microns).

While the above description has been directed to a container in the form of a bag, the container may take other forms as well. For example, the container might be in the form of a drum on a rigid carton. These forms generally allow for larger individual packaging, the drum often holding amounts of up to about 250 pounds (113 kg) of product while the rigid carton is normally intended for bulk shipments of 500 pounds (227 kg) or more.

The following examples are merely illustrative and are not to be construed as limiting the invention, the scope of which is defined by the appended claims.

Example 1

A quantity of 200 g of freshly dried anhydrous fine granular citric acid having a moisture content of 0.1 weight percent was placed in each of three 8 oz glass

bottles, filling the bottle to about 75 percent of its capacity. In addition, the following were added to the bottles:

Bottle A - nothing;

Bottle B - a 1-g section of a 5-ply kraft paper bag; and

Bottle C - a 1-g section of a 5-ply kraft paper as with bottle B but previously dried for about 16 hours at 110°C.

Each of the bottles was sealed with a plastic screw cap and further sealed by dipping the cap and top of the bottle into molten wax. The bottles were then stored under ambient conditions for 5 days and examined with the following observations:

Bottle A - contained essentially one 200 g lump which did not move upon inversion of the bottle and which required considerable shaking to make free flowing;

Bottle B - contained a lump similar to bottle A which required slightly less shaking to make free flowing;

Bottle C - contents completely free flowing and lump free.

The experiment is repeated substituting either anhydrous sodium citrate or potassium citrate for the anhydrous citric acid with essentially the same results.

Example 2

A production lot of fine granular anhydrous citric acid dried atmospherically at 115-130°C to a moisture content of about 0.1 weight percent was packaged while still warm in 100-lb (45-kg) 5-ply kraft paper bags. These bags were constructed with an inner layer of 3 plys of 50 pound basis natural kraft paper and an outer layer of 1.5-mil (38-micron) LPDE film faced on its outer surface with a layer consisting of a single ply of 50 pound basis and a single ply of 60 pound basis natural kraft paper. A portion of the packaging was done in bags which were previously dried in a forced circulation air dryer operating at 130-150°F (54-66°C) to reduce the moisture content of the paper to about 2 to 3 percent by weight below the equilibrium moisture content of the paper, while the remainder was packaged in the bags as received. Examination of the packaged lot after five months of storage at ambient conditions indicated that the portion packaged in the dried bags was still free flowing, while the remainder packaged in the bags as received had caked.

Example 3

A bag for the packaging and storage of 100-lb (45-kg) quantities of anhydrous particulate citric acid is fabricated with an outer layer of 2-mil (51-micron) HDPE faced on its outer surface with a single ply of 60 pound basis natural kraft paper and an inner layer of 4 plys of 50 pound basis natural kraft paper and an inner layer of 4 plys of 50 pound basis natural kraft paper faced on its inner surface with a 2-mil (51-micron) film of Tyvek 1073B. The bags are placed in a forced circulation air dryer operating st 130-150°F (54-66°C) to reduce the moisture content of the inner paper layer from the equilibrium value of 7 to a value of 2 percent by weight. Freshly dried production particulate anhydrous citric acid is introduced into the bag and the bag is sealed. The sealed bag is stored at ambient conditions of 70-90°F (21-32°C) and 50-70 percent relative humidity. Examination of the bag and its contents after three months of storage indicates the citric acid to be completely free flowing with essentially no retention of the product in the bag when the product is poured from the bag.

Similar results are obtained when the bag is fabricated with an outer layer of a laminate of aluminum foil between HDPE having a thickness of 1 mil (25 microns) faced with a single ply of 60 pound basis bleached kraft paper and the inner layer is 4 plys of 50 pound basis natural kraft paper faced with a porous coating of polyethylene.

CLAIMS

1. A multilayered container for the storage of particulate hygroscopic substances which comprises an outer layer having a low WVTR and an inner layer of at least one thickness of paper having a moisture content significantly below said paper's equilibrium moisture content whereby said inner layer acts as a desiccant for said hygroscopic sustances.

2. The container of Claim 1 wherein said outer layer comprises aluminum foil or polyethylene film.

3. The container of Claim 1 wherein the outer surface of said outer layer is faced with a layer of paper.

4. The container of Claim 1 wherein theinner surface of said inner layer is faced with a water vapor-permeable layer of hydrophobic material.

5. The container of Claim 4 wherein said material is polyethylene.

6. The container of Claim 1 wherein the moisture content of said paper is about 2 to 5 percent by weight below said paper's equilibrium moisture content.

7. The container of Claim 1 wherein said container is in the form of a bag.

8. The container of Claim 1 wherein said hygroscopic substance is anhydrous citric acid.

9. A method for the packaging of particulate anhydrous citric acid which comprises:

a. preparing a multilayered bag comprising an outer layer of low WVTR polyethylene film and an inner layer of at least one thickness of paper faced with a water vapor-permeable layer of polyethylene on the inner surface of said paper layer;

b. reducing the moisture content of said paper in said bag to about 2 to 5 percent by weight below said paper's equilibrium moisture content;

c. introducing said citric acid into said bag and

d. sealing said bag.

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